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16. ABSTRACT

A method is described for analysis of complex industrial and municipal wastes. The method uses chemical fractionation and subfractionation combined with laboratory toxicity tests on marine and freshwater algae and crustaceans to determine toxicity of whole waste and to identify its toxic components. Endpoints are stimulation or inhibition of algal population growth and death of crustaceans. Algae are particularly good indicators of bioactivity, often reacting to growth stimulants at low concentrations (less than 0.1%) and to toxicants at higher concentrations in a single waste. Effects of bioactive substances may be suppressed by other bioactive substances, and fractionation often reveals effects not found in tests with raw waste. After identification of toxic fractions and subfractions, production and treatment systems can be modified to eliminate specific toxicants, thus saving the considerable cost of whole waste treatment.

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POLLUTANT SORPTION IN ENVIRONMENTAL SYSTEMS

by

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16. ABSTRACT

The development of mathematical models of sorptive processes affecting pollutant fate in aquatic systems is reviewed. The review discusses research on equilibrium sorption (partition coefficient), soil and sediment sorption of uncharged organics (dependence on organic carbon), estimation of fugacity coefficient ratio ($K_{}$), hydrophobic sorption, sorption to microorganisms and dissolved humics, non-hydrophobic bonding, sorption kinetics and bioconcentration.

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CHAPTER 3

POLLUTANT SORPTION IN ENVIRONMENTAL SYSTEMS

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Table of Contents

I. Introduction

II. Equilibrium Sorption -- Partition Coefficient

III. Soil and Sediment Sorption of Uncharged Organics-- Dependence on Organic Carbon

IV. Estimation of K_{oc}

A. K_{oc} from Water Solubility

B. K_{oc} from K_{ow}

C. A priori K_{oc} Estimation from Molecular Fragments

D. K_{oc} Estimates for Benchmark Compounds

V. Gel Permeation Model for Hydrophobic Sorption

VI. Sorption to Microorganisms and Dissolved Humics

VII. Non-hydrophobic Bonding

VIII. Sorption Kinetics

IX. Bioconcentration

X. References

I. INTRODUCTION

Pollutant fate in an environmental system is highly dependent on sorptive behavior. In addition to an obvious effect on physical transport, sorption can be involved directly or indirectly in pollutant degradation. The chemical reactivity of a pollutant in a sorbed state may differ significantly from that in aqueous solution, both in extent and chemical pathway.[1-4] Moreover, natural sorbents may indirectly mediate solution phase processes by altering the solution phase pollutant concentration, or by controlling pollutant release into the aqueous phase and thereby potentially rate-limiting the solution phase reaction. In addition, natural sorbents "introduce" into solution a "buffered" suite of inorganic and organic species that may significantly affect pollutant reactivity in the aqueous phase. An understanding of these sorptive processes is an important key to describing pollutant fate in aquatic systems.

Natural sorbents may be biotic and abiotic, may be organic, inorganic, or chemical composites thereof and may range in size from macromolecules to gravel. Organic pollutants vary in size (single carbon to macromolecular compounds) and in water solubility from complete miscibility to virtual insolubility. This high degree of variability and complexity in sorbent/sorbate composition, chemical character, and potential sorptive interactions seems to preclude the development of simplistic sorption models with any degree of theoretical legitimacy. The key to such model development involves discriminating initially the essential phenomenological behavior (trends) while neglecting what could be termed "second-order" effects or incidental details. These "idealized" models can then be made more general by the addition of "corrective terms" that hopefully can be causally related to those details neglected in the idealization process.

A fundamental prerequisite to model development is definition of purpose. Model structure (i.e., mathematical format and degree of abstraction, level of temporal and spatial detail, and requirement for supporting physical rationale) is intimately a function of intended use. The sorption models described herein are designed for what might be loosely characterized as engineering applications and can serve the following purposes:

(1) a priori estimation of pollutant sorption behavior using commonly measured (or computed) physical properties of pollutant and sorbent and incorporating commonly measured environmental variables.

(2) guidance for ordering, interpreting and, in a non-rigorous sense, "understanding" existing data.

(3) evaluation or screening of existing data based on "expected" behavior.

(4) extrapolation of sorption measurements (field or laboratory) outside the domain of measurement.

For the most part, model validity derives more from long-term accretion of phenomenological evidence than from mechanistic rigor. Physical rationale is offered, however, in support of mathematical functionality, and is used to define (or extend) appropriate models in instances where the current state of knowledge or available data are insufficient for model definition. It should be stated at the outset that the prescribed usage precludes the utilization of regression equations developed and calibrated for site-specific circumstances.

II. EQUILIBRIUM SORPTION - PARTITION COEFFICIENT

Equilibrium sorption is described graphically by a sorption isotherm, which is a plot of pollutant concentration in the sorbed phase (denoted C_s)

versus pollutant concentration in solution (C_w). Sorption isotherms are typically measured at constant temperature and at constant sorbent concentration.

Thermodynamically, sorption equilibrium can be defined as the state at which the pollutant fugacities in the sorbed and solution phases are equal

$$f_s = f_w \qquad (1)$$

where the subscripts s and w refer to the sorbed and solution phases, respectively. (Mackay[5,6] has described the use of fugacity in environmental systems.)

Moreover, even if the sorbent, such as a soil or sediment, is pictured as a composite mixture of different sorbents, the fugacity within each sorptive compartment must be equal at equilibrium.

$$f_{s_i} = f_w \text{ for all sorptive compartments (i).}$$

The fugacity or "escaping tendency" can be related to pollutant concentration in each phase. For example, for the aqueous phase,

$$f_w = \phi_w C_w \qquad (2)$$

The fugacity coefficient (ϕ_w, ϕ_s) is commonly expressed as the product of an activity coefficient (γ) and the corresponding reference state fugacity (f^o). This fugacity coefficient is the reciprocal of the fugacity capacity used by Mackay.[5,6] For example,

$$\phi_w = \gamma_w f_w^o \qquad (3)$$

The numerical evaluation of any given coefficient (ϕ) requires the specification of the standard or reference state and its associated

fugacity. Aqueous phase pollutant concentrations are conventionally expressed relative to aqueous phase volume, and sorbed concentrations are referenced to dry mass sediment/soil.

For the sorbent "mixture," the sorbed pollutant concentration can be taken as a weight-averaged sum of the components.

$$C_s = \sum_i Y_i C_{s_i} = f_s \sum_i \frac{Y_i}{\phi_{s_i}} \tag{4}$$

where Y_i denote component weight fractions. The sorbed and solution pollutant concentrations are related by

$$C_s = C_w \frac{\phi_w}{\phi_s} \tag{5}$$

In general, fugacity coefficients are dependent on pollutant concentration and, therefore, the corresponding sorption isotherms are nonlinear. In sufficiently dilute systems, however, these coefficients approach limiting values and the isotherms approach linearity. In simplistic terms, this is the limit in which solute-solute interactions can be ignored in each phase; the molecular environment of the pollutant within each phase remains relatively constant with changes in solute concentration. It is this "low loading" limit that should be quite typical of most environmental situations,

$$C_s = K_{sw} C_w \tag{6}$$

where

$$K_{sw} = \frac{\phi_w}{\phi_s} \quad \text{or} \quad K_{sw} = \phi_w \sum_i \frac{Y_i}{\phi_{s_i}} \quad \text{(for composite sorbents)} \tag{7}$$

K_{sw} is the sorption partition coefficient, and the fugacity coefficients are low-concentration limiting values. By convention, concentration units are chosen with the volume unit in solution equivalent in mass to the mass

unit for sediment; typical units for K_{sw} are therefore l/kg or ml/g.

How dilute the system must be to show this limiting behavior varies from system to system, depending on the nature of the solute and sorbent and on the type of sorption interaction. Just as in gas-liquid equilibria, where rough rules for adherence to Henry's law can be formulated in terms of solute solubilities and partial pressures,[7] it has been determined[8] for hydrophobic compounds that, if the equilibrium aqueous phase pollutant concentration is below 10^{-5} mole/liter or less than one half of the solute water solubility (whichever is lower), sorption isotherms to natural sediments are linear. More recent works[9-15] substantiate this low-loading isotherm linearity for hydrophobic compounds. For non-hydrophobic bonding, low-loading isotherm linearity is frequently observed also.[16] Unfortunately, conditions for linearity may involve sorbent and solution phase chemistry in addition to pollutant loading and, therefore, cannot be specified as simply as in the "hydrophobics" case. (This is discussed in subsequent sections.) A potentially important source of observed isotherm non-linearity is solute speciation changes (aggregation, proton gain or loss, chemical complexation or degradation) not explicity accounted for or experimentally measured or controlled.

It should be emphasized that "sorbed state" concentrations, and thermodynamic variables derived therefrom, are operationally defined. Sorbed concentrations are commonly referenced to total sorbent mass (as specified for C_s) or to the mass of a specific component of the sorbent (i.e., C_{s_i}). Seldom can the actual distribution volume of the sorbate be defined; nor is the uniformity or anisotropy of the sorbate distribution typically known. Thermodynamic properties derived from these measurements are highly dependent in numerical value on computational prescription and

care must be exercised in mechanistic implications derived therefrom. Exceptions are thermodynamic properties pertaining to the sorbed state but fixed in value, relative to the aqueous phase, by equilibrium constraints (i.e., chemical potential, fugacity, temperature, etc.).

III. SOIL AND SEDIMENT SORPTION OF UNCHARGED ORGANIC CHEMICALS--DEPENDENCE ON ORGANIC CARBON

From pesticide-soil studies, numerous soil properties [organic carbon content, particle size distribution, clay mineral composition (amount and type), pH, cation-exchange capacity (CEC)] have been identified as affecting the type (mechanism) and/or degree of pesticide sorption.[16-27] However, the predominance of organic carbon in "controlling" the sorption of uncharged organic compounds has been extensively documented for soils[10,15,18,26-30] and more recently confirmed for sediments.[8,9,12,31-33] This suggests that the partition coefficient for a soil or sediment consisting of multiple sorbent components (i.e., eq. 7) can be reduced (in a first approximation) to a form containing only sorption to organic matter.

$$K_{sw} \simeq \phi_w \frac{oc}{\phi_{oc}} \tag{8}$$

where organic matter is expressed as fraction organic carbon, oc. The fugacity coefficient ratio is typically defined as K_{oc}.

$$K_{oc} \simeq \frac{\phi_w}{\phi_{oc}} \tag{9}$$

"Carbon-referenced sorption" has been tested for a wide variety of both compounds and sediment/soils. Most notable documentation is contained in Walker and Crawford[30] (triazines, 32 soils), Talbert and Fletchall[25] (triazines, 25 soils), Karickhoff[31] (polynuclear aromatics, 17 sediments/soils), and Hassett et al.[12] (polynuclear aromatic and related heterocyclic

organics, 14 sediments/soils). From these findings, combined with the data compilations on pesticide/soil sorption by Rao et al.[29] and Farmer[34], it can be safely generalized that, for uncharged organic compounds of limited water solubility (<10^{-3} mole/liter) that are not susceptible to speciation changes or other special complex formation in the sediment or soil suspension of interest, sorption is typically "controlled" by organic carbon and is amenable to the K_{OC} format of quantification.

IV. ESTIMATION OF K_{OC}

As described in the previous section, K_{SW} estimation for uncharged organics can typically be reduced to estimation of K_{OC}, which, when combined with organic carbon content, can yield a good estimate of the sediment- or soil-water partition coefficient (K_{SW}) (eq's 8 & 9). The K_{OC} can be expressed as the ratio of solute fugacity coefficients in the aqueous, ϕ_W, and organic matter, ϕ_{OC}, phases (eq 9) or in terms of activity coefficients,

$$K_{OC} \propto \frac{\gamma_W}{\gamma_{OC}} \qquad (10)$$

where the proportionality constant contains the reference state fugacity and unit conversion factors for pollutant concentrations. For hydrophobic materials, a convenient reference state is the pure liquid (or subcooled liquid at STP). Because the activity coefficient "contrasts" adhesive (solvent-solute) and cohesive (i.e., solute-solute) interactions in a given phase with the cohesive interactions in the solute reference state (i.e., pure liquid), one would expect highly nonideal behavior in the aqueous phase with large variations in γ_W from solute to solute (comparable to differences in aqueous phase solubility). To the contrary, in the sorbed state the adhesive (i.e., sorptive) interactions with the organic

matrix could be assumed to be quite similar in type and magnitude to cohesive interactions in the pollutant reference state. Variations in γ_{oc} from solute to solute would be largely entropic in nature and would be comparable to changes in solute molar volume (as prescribed by the Flory-Huggins relationship[35]). In going from benzene to benzpyrene, for example, one would expect approximately a fourfold increase in γ_{oc} compared to an increase in γ_w of roughly four orders of magnitude. Thus, for a series of hydrophobic organics, variations in K_{oc} would be dominated by variations in the aqueous phase activity coefficient.

$$K_{oc} \propto \gamma_w \tag{11}$$

A. K_{oc} from Water Solubility. For hydrophobic liquids, γ_w is equal to the reciprocal of the mole fraction solubility, SOL. For solids, a crystal energy term must be added, which gives in an approximated form (see Prausnitz[7] for a more complete expression):

$$\log \gamma_w = -\log SOL - \frac{\Delta S_f (T_m - T)}{2.303\ RT} \tag{12}$$

where ΔS_f is the solute entropy of fusion, T_m is the melting point in °K, T is absolute temperature, and R is the gas constant. For liquids (i.e., $T > T_m$), T is set equal to T_m and the crystal term vanishes. Yalkowsky and Valvani[36,37] have discussed, in detail, estimation of ΔS_f. For "rigid" organic molecules that are solids at 25°C, ΔS_f is not highly variable, 12-15 eu (entropy units, cal/deg mole). Rigid molecules include cyclic compounds (aliphatic or aromatic) and molecules containing less than five atoms in a flexible chain. Fortunately, nonrigid molecules typically melt at much lower temperatures than rigid molecules of similar molecular weight and are frequently liquids at room temperature; for these compounds, the

"crystal term" is either zero or very small in most instances.

Expressing γ_{oc} in terms of readily accessible molecular properties is not so straightforward. With regard to K_{oc} estimation, however, variation in γ_{oc} from solute to solute is presumed to be of secondary importance and can be implicitly factored into the solubility dependence, by empirically fitting observed sorption data to an equation of the form

$$\log K_{oc} = - \alpha \log SOL - \frac{\Delta Sf(T_m-T)}{2.303\ RT} + \beta \qquad (13)$$

where α and β are regression-fitted parameters. The deviation of α from unity reflects variation in γ_{oc} for the basis set of compounds.

An equation of this form has been applied to condensed ring aromatics[31] giving:

$$\log K_{oc} = -0.921 \log SOL -0.00953(mp-25)-1.405 \qquad (14)$$

where ΔS_f is taken to be 13.0 eu; mp is the melting point in °C. This equation was examined using literature data for other families of hydrophobic organics (triazines, carbamates, organophosphates, chlorinated hydrocarbons) and was found to estimate K_{oc} generally within a factor of 2 to 3 of measured values. For chlorinated hydrocarbons, however, the equation worked well for low molecular weight compounds (both aliphatic and aromatic) but tended to overestimate (by as much as an order of magnitude) sorption of highly chlorinated, high molecular weight compounds (such as DDT or hexachlorobiphenyls). This suggests that the α coefficient (equation 13) for this class of compounds would be considerably less than the polynuclear-aromatic-hydrocarbon (PNA) value, apparently in the range 0.7 to 0.8. It is uncertain whether this deviation derives from kinetic or steric inhibition

of sorption or decreased affinity for natural organic matter (i.e., increase in γ_{oc}). Recent studies with these types of compounds,[3-41] however, found a significant increase in sorption at low solids concentrations ($< 10^{-4}$ g/ml), with K_{oc}'s (determined at low solids) corresponding much more closely with estimated values. For these types of compounds, sorbent access may be an important factor. If the literature data (catalogued in Karickhoff[31]) for five chemical families are fitted to equation 12, the resulting equation is

$$\log K_{oc} = -0.83 \log SOL - 0.01(mp-25) - 0.93 \quad (47 \text{ compounds}, r^2 = 0.93) \tag{15}$$

B. K_{oc} From K_{ow}. The octanol/water partition coefficient (K_{ow}) like K_{oc} is a distribution coefficient of solute monomers between an aqueous phase and a hydrophobic organic phase. Thermodynamically K_{ow} can be expressed as the ratio of activity coefficients if the same standard state is chosen in each phase (i.e., pure subcooled liquid solute).

$$K_{ow} = \frac{C_o}{C_w} = \frac{\phi_w}{\phi_o} = \beta \frac{\gamma_w}{\gamma_o} \tag{16}$$

where o and w denote the octanol and aqueous phases, respectively; β is a unit adjustment constant converting C_o and C_w to mole fraction units in each phase. As was the case in sediment/water systems, γ_w can be considered to be the distilled water activity coefficient, unaffected by the presence of octanol (approximately 10^{-3} mole/liter at 25°C) in the aqueous phase.

By combining equations 9 and 16, K_{oc} and K_{ow} are related by

$$K_{oc} = \frac{\phi_o}{\phi_{oc}} K_{ow} \tag{17}$$

where the proportionality constant is the ratio of fugacity coefficients for the solute dissolved in octanol (saturated with water) and bound in natural organic matter. For K_{oc} and K_{ow} to be linearly related, this ratio must be independent of solute.

In numerous studies involving a wide variety of chemicals, the correlation line between K_{oc} and K_{ow} has been examined.[8,9,12,28,29,31-33,42,43] Typically a linear regression equation of the following form is used:

$$\log K_{oc} = \alpha \log K_{ow} + \beta \qquad (18)$$

where α and β are data-fitted coefficients. The result is a somewhat divergent group of relationships. Several factors contribute to this variability:

(1) hydrophilic contributions to sorption--the thermodynamic rationale for relating K_{oc} to K_{ow} is predicated on (a) the predominance of organic carbon as the key sorbent component of soils and sediments, (b) the predominance of hydrophobic sorption (as opposed to polar group interactions, ionic bonding, or chemisorption), and (c) sorption linearity. The impact of hydrophilic factors on the observed K_{oc} is more in evidence for molecules containing polar functional groups, which tend to be those with lower K_{ow}'s (10^3 or less).

(2) kinetic or steric inhibition of sorption--for many sorbate/sediment systems true sorption equilibrium may require weeks or longer. The phenomenon appears to be one of solute access to sorbent and is especially in evidence for large molecules. Solids concentration and composition (cohesive properties) appear to "govern" sorbent access. The net effect is an apparent reduction in K_{oc} when sorption is measured over short time frames (hours).

(3) use of computed K_{ow}'s--substituent or fragment constants

determined for small or monosubstituted molecules frequently do not work well for either large molecules or molecules with multiple substituents, resulting frequently in overestimates of K_{ow}.

The combined effect of these factors is illustrated in Figure 1 where deviations from hydrophobic sorption are indicated by hatched areas.

Published equations "calibrated" on sets of hydrophobic compounds include:

-- $\log K_{oc} = 0.72 \log K_{ow} + 0.49$ (predominantly methylated and halogenated benzenes, 13 compounds, $r^2 = 0.95$)[33] (19)

-- $\log K_{oc} = 1.029 \log K_{ow} - 0.18$ (13 pesticides, $r^2 = 0.91$)[29] (20)

-- $\log K_{oc} = 0.989 \log K_{ow} - 0.346$ (5 PNA's, $r^2 = 0.997$)[31] (21)

-- $\log K_{oc} = \log K_{ow} - 0.317$ (PNA's and substituted PNA's, 22 compounds, $r^2 = 0.98$).[12] (22)

C. A priori K_{oc} Estimation from Molecular Fragments. For computing thermodynamic properties, it has often been found useful to consider a molecule as a collection of molecular fragments, each making a distinct contribution to the thermodynamic property, which is relatively independent of the rest of the molecule. The most common application of this general concept is Linear Free Energy Theory (LFET), which frequently has been applied to solute partitioning between phases (i.e., chromatography,[44] octanol/water partitioning[45,46] and even sorption to soils[47]). The rationale behind the method is that a large number of molecular structures can be generated from a relatively small number of fragments, and thus a larger number of thermodynamic estimates can result from a small number of experimental measurements (fragment constants). The accuracy of the prediction, however, necessarily improves as the specificity of the

fragment environment increases, which entails an increase in the number of fragments (or corrective factors) that must be considered. Practicality necessitates a compromise. In any given application, this theory is applied at different levels of sophistication. One user may employ a few fragment constants and generate "first order" estimates whereas another may employ numerous corrections or adjustments reflecting more fragment specificity for a given molecular environment. For multiply substituted compounds, good estimates generally require sophisticated input, either in terms of system specific fragment constants or corrective terms. This approach, however, can permit facile extrapolation of K_{oc} measurements in some instances.

1. Addition of ring fragments. For unsubstituted condensed ring aromatics, one can write

$$f^{\alpha}_{C_4H_2} = \log K_{oc}\text{ (naphthalene)} - \log K_{oc}\text{ (benzene)} \qquad (23)$$
$$\approx 1.16^{31}$$

where $f^{\alpha}_{C_4H_2}$ denotes the ring fragment constant for α condensed ring addition (i.e., fragment attached at α carbons). With this fragment constant, one can extrapolate to other condensed ring systems. For 3-ring systems, phenanthrene and anthracene, the computed value is 4.10 compared to the measured log K_{oc}'s of 4.03 and 4.20,[31] respectively. For 4 and 5-ring systems, the computed values are 5.26 and 6.42; measured values are 5.81[8] for tetracene (4 ring) and 6.22[12] for dibenz[a,h] anthracene (5 ring). Similarly, fragment constants can be derived for ring addition involving three carbon addition (β condensation) and two carbon addition (γ condensation), which would enable K_{oc} estimation for most condensed (6 membered ring) aromatic hydrocarbons.

2. Addition of functional groups. The addition of a functional group [(X) (replacing a H atom)] to a hydrocarbon matrix (R-H) is a primary application of LFET. In this case

$$\log K_{oc}(R\text{-}X) - \log K_{oc}(R\text{-}H) = \pi_x^s \qquad (24)$$

The substituent constants, π_x^s are determined experimentally and are relatively system independent for similar organic molecules. System specificity can be especially large for (a) addition of polar functional groups - NH_2 and - OH, (b) addition of electron releasing or withdrawing groups to compounds that can potentially ionize in sediment/water systems, and (c) multiple substitution of functional groups on a hydrocarbon matrix. Although this approach is not easily adaptable to a priori estimation of K_{oc} for most pesticides, it does offer considerable potential for mono- and di-substituted compounds. In this respect, tremendous advantage can be derived from the relationship between K_{oc} and K_{ow} described in the previous section (eqs. 17-22). Because K_{oc} and K_{ow} are approximately linearly related, it can easily be shown that the substituent constants, π_x^s, for sorption approximate those for the comparable K_{ow} system, π_x^o. This makes possible the the use of this extrapolation procedure without development of an extensive library of substituent constants, π_x^s. The comparable K_{ow} constants, π_x^o, are readily available[45,46] and are generally applicable excepting those instances described previously. It should be emphasized that this extrapolation does not require a knowledge of K_{ow} for either of the specific compounds R-H or R-X in question.

For example,

$$\log K_{oc} \text{ (chlorobenzene)} \simeq \log K_{oc} \text{ (benzene)} + \pi^{\circ}_{Cl} \qquad (25)$$

$$\pi^{\circ}_{Cl} = 0.71^{46}$$

Therefore,

$$\log K_{oc} \text{ (chlorobenzene)} \simeq 1.78 + 0.71 = 2.49 \qquad (26)$$

D. K_{oc} Estimates for Benchmark Compounds. Table 1 lists K_{oc} estimates derived from SOL and K_{ow}. Unfortunately, few literature sorption data are available for comparison. Where available, measured values compare with estimates generally to within measurement error or expected field sample variability.

V. GEL PERMEATION MODEL FOR HYDROPHOBIC SORPTION

Recently, Freeman and Cheung (17) have applied solubility parameter theory to organic carbon-controlled sorption to natural sediments. Natural organic matter in sediment was pictured as a humic-kerogen gel affixed to mineral surfaces, and sorptive processes (kinetic and equilibrium) were described in terms of the diphasic liquid-gel-solute interactions.

$$\ln K_{oc} = A - BL_i + \frac{V_i}{RT} f(\delta) \qquad (27)$$

where the sediment parameters A and B depend upon pore structure within the sorbent gel, L_i is the size of the solute, V_i is the solute molar volume, and $f(\delta)$ is the solubility parameter function that expresses the solute preference for the liquid versus gel phases as given by

$$f(\delta) = (\delta_i - \delta_m)^2 - (\delta_i - \delta_g)^2 \qquad (28)$$

where the subscripts i, m, g denote the solute, solvent and gel phases, respectively. This approach has been applied to only one sediment, and

thus the sediment variability of A, B, and δ_g has not been determined. Also, there is a paucity of solubility parameter data for pollutants. A most notable advantage of this approach is the facile extension to non-aqueous or mixed solvents, requiring only the adjustment of the solvent solubility parameter, δ_m.

VI. SORPTION TO MICROORGANISMS AND DISSOLVED HUMICS

For hydrophobic organics, sorption to microorganisms and/or colloidal humic material is amenable to this same thermodynamic treatment and should lead to similar estimation equations. Relationships have been developed for mixed microbial populations, relating sorption to both water solubility and octanol/ water partition coefficients.[48,49] It is noteworthy that if sorption is referenced to carbon (as opposed to bacterial mass), partition coefficients to bacteria approximate sediment derived K_{oc}'s.

In the case of "prepared" humics (i.e., isolated from soil/sediment aggregates), "sorption" appears sensitive to both the source and mode of preparation.[50-54] Insufficient data exist to formulate estimation equations, but octanol/water partition coefficients can be taken as numerical upper limits for association of hydrophobic pollutants to natural humics.

VII. NON-HYDROPHOBIC BONDING

For the vast majority of uncharged pollutants, "carbon referenced" sorption is appropriate and the estimation techniques detailed previously for hydrophobic sorption give good estimates of "low loading" linear partition coefficients for natural soils/sediments. Non-hydrophobic interactions may contribute to (or dominate) sorption in some instances, however, a point that was stressed in a recent review by Mingelgrin and Gerstl.[16] This tends to occur in coincidence with one or more of the

following conditions:

(1) high sorbate polarity--highly polar and/or ionizable functional groups conducive to significant site-specific bonding with polar groups or charged sites on sorbent surfaces.

(2) low organic carbon content in the sorbent, especially with coincident high clay content.

(3) low soil moisture content.

Unfortunately, the state-of-science does not permit a priori sorption estimation, comparable to hydrophobic bonding in this instance. Recently a prescriptive format has been offered for a logical mathematical approach, and specific examples were discussed where quantification is possible.[55]

VIII. SORPTION KINETICS

A great deal of confusion exists in the sorption literature regarding the speed of attainment of sorption equilibrium. Sorption is often described as rapid and readily reversible (times to reach equilibrium of minutes to a few hours). Yet analytical chemists commonly encounter extreme difficulty extracting pollutants from field soils or sediments. For example, quantitative recovery of paraquat from a field soil requires, in effect, "dissolution" of the sorbent matrix to achieve chemical release.[24] Similarly, highly sorbed hydrophobic compounds frequently require lengthy extraction periods (days), multiple solvents, abrasive mixing techniques (or a combination thereof) for quantitative chemical recovery.

A concept long held by soil chemists (see Rao et al.[29,56] for a discussion of isotherm nonsingularity), and recently revamped for pollutant sorption to sediments,[38] distinguishes the relative rates of the forward (adsorption) versus the reverse (desorption) process. DiToro and Horzempa[38] found for the sorption of a hexachlorobiphenyl to various sorbents (sediments,

clays, silica) that the adsorption process was rapid (minutes to hours), but for the reverse process, a significant portion (~ 0.5) of the sorbed chemical was highly "resistant" to release. Conventional partition coefficients were factored into reversible and release-resistant components, based on hysteresis analysis.

Karickhoff[57] reported a somewhat similar finding for polynuclear aromatic hydrocarbons where the adsorption process appeared very rapid--that is, 35-60% of the equilibrium sorption was achieved in minutes (mixing limited) with apparent equilibrium after a few hours. Also, a drastic change in the ease of extraction of sorbed chemical was frequently observed with increased incubation time. After short incubation periods (< 5 minutes) essentially all (> 90%) of the sorbed chemicals could be easily extracted from the sediments by direct extraction of the suspensions with hexane for approximately 3 minutes. The fraction of sorbed chemical recovered by this brief extraction decreased to 0.5 after 3-5 hours of incubation and continued to decrease slowly over the next few days, leveling out in the range 0.2 to 0.4.

All of these findings are suggestive of a diffusion controlled process in the sorbed state where sorbed chemical is slowly incorporated into either porous aggregates or sorbent components. If one measures changes in aqueous phase and/or sorbed phase concentrations, the process appears to be complete after a few hours, but in reality may proceed indefinitely. As mentioned previously, both solids concentration and composition appear to affect significantly the uptake or release kinetics of sorbed pollutants.

Current knowledge of this process (or processes) is incomplete or in some cases conflicting, but this author is very perplexed by the failure

of most sorption reports to acknowledge any evidence of a "resistant" sorption component.

IX. BIOCONCENTRATION

Pollutant uptake by higher order aquatic animals can be viewed in much the same manner as sorption to sediments, bacteria, etc. That is, fish (or other aquatic animals) will accumulate or discharge chemicals in accordance with the pollutant fugacity differential within the organism relative to the external environment. Continuous exposure to a relatively constant pollutant source will result in an "equilibrium" condition (barring kinetic constraints) analogous to sorption equilibria described previously. That is,

$$K_{fi} \equiv \frac{C_f}{C_i} \tag{29}$$

where K_{fi} is the equilibrium distribution coefficient, C_f and C_i are pollutant concentrations in the fish (dry mass referenced) and pollutant source, respectively. The pollutant concentration in the fish relative to the surrounding water is defined as the "biological concentration factor" (denoted BCF).

As was done previously for composite sediments, it is sometimes convenient to factor the organism into independent distribution volumes (corresponding to distinct types of tissue).

The distribution coefficient can be expressed as

$$K_{fi} = \frac{1}{C_i} \sum_j Y_j C_{fj} \tag{30}$$

where C_{fj} are pollutant concentrations in individual tissues and Y_j are the corresponding component weight fractions. Frequently, pollutants concentrate in a few tissues or in some cases can be localized in a single

tissue. In this case

$$K_{fi} \approx Y_j \quad C_{fj}/C_i \qquad (31)$$

The concentration ratio C_{fj}/C_i may then constitute a "benchmark" distribution coefficient (analogous to K_{oc}) and Y_j may serve as a normalizing factor for bioconcentration in different individuals or different species. Lipid content frequently is considered in this regard for bioconcentration of hydrophobic pollutants.

The tendency of nonpolar pollutants to bioconcentrate in animal tissue relative to water has been frequently related to "hydrophobicity" (i.e., the K_{ow} or water solubility of the compound). Regression equations relating bioconcentration to these physical properties are widespread in the literature and have been recently summarized by Bysshe.[58] At the present time these equations provide the best estimation of bioconcentration potential.

Aquatic animals do not always behave as "passive sponges" in regard to pollutant uptake and release. Larger pollutant molecules may be transport-limited (both in entering and translocating within the animal) whereas other chemicals may be chemically changed (reversibly or irreversibly) within the animal. Under these conditions, bioconcentration should be expressed dynamically, and the time rate of change of pollutant concentration in the animal given by

$$\frac{dC_f}{dt} = \sum_i k_i C_i - \sum_i k_j C_f \qquad (32)$$

where the subscript i denotes pollutant uptake sources or modes of uptake and the subscript j denotes chemical clearance pathways (excretion or

chemical degradation). All processes are generally considered to be independent and first-order in chemical concentration(s) (i.e., the k's are independent of pollutant concentration). The kinetic coefficients incorporate organism physiology as well as chemical uptake "efficiency" (affinity plus transport limitations) and are generally expressed in factored form. For example, the kinetic coefficient for pollutant uptake from water via the gill is given by

$$k_w \equiv \text{Volume of water filtered per unit fish mass per unit time} \times \text{efficiency of chemical absorption across gill} \tag{33}$$

Likewise, uptake via fish prey is given by

$$k_p \equiv \text{mass of food ingested per unit fish mass per unit time} \times \text{efficiency of chemical absorption} \tag{34}$$

Neely[59] recently addressed estimation of these factored contributions to chemical uptake via fish gills.

For prolonged organism exposure to a relatively constant source(s) of pollutants, the concentration within the organism will achieve some steady-state value, given by

$$C_f = \sum_i k_i C_i \Big/ \sum_j k_j \tag{35}$$

Under these conditions, the bioconcentration factor is given by

$$BCF = \frac{1}{\Sigma k_j} \sum_i k_i C_i/C_w \tag{36}$$

If chemical equilibrium exists among sources (i.e. constant pollutant fugacity in all pollutant sources), the BCF is given by

$$BCF = \frac{1}{\Sigma k_j} \sum_i k_i K_{iw} \tag{37}$$

where K_{iw} is the pollutant distribution coefficient for pollutant

concentration in source i, relative to water (i.e., $C_i = K_{iw}C_w$; $K_{ww} \equiv 1$).

These equations facilitate the direct comparison of multiple sources and/or modes of chemical uptake. Current apporoaches[59,60] in studying bioconcentration are moving toward evaluating process dynamics in pollutant uptake and clearance.

Figure Captions

Figure 1 K_{oc} : Extrapolation from K_{ow}

Figure 1

K_{oc} : Extrapolation from K_{ow}

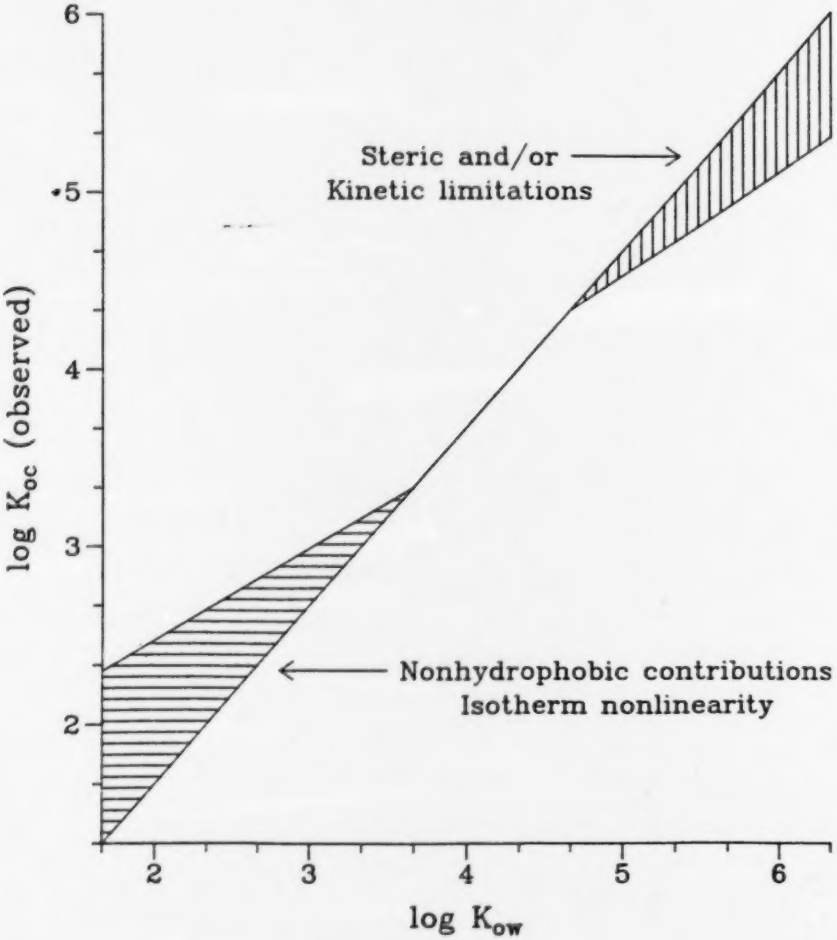

Table 1 Benchmark Chemicals -- K_{oc} Estimates

Chemical	Measured Properties			Estimated log K_{oc}						
	log K_{ow}	-log SOL (mole fraction)	log K_{oc}	from K_{ow} (eq. 19)	from K_{ow} (eq. 20)	from K_{ow} (eq. 21)	from K_{ow} (eq. 22)	from SOL (eq. 14)	from SOL (eq. 15)	best estimate[b]
methyl chloroform	2.47(61)	3.74(61) 4.01(a)	2.25(63)	2.27	2.36	2.08	2.15	2.04 2.28	2.17 2.40	2.2
freon	2.53(62)	3.84(a)		2.31	2.42	2.16	2.21	2.13	2.26	2.2
chlorobenzene	2.84(46)	4.11(a)		2.53	2.85	2.46	2.52	2.38	2.48	2.5(c)
1,2,4 trichloro-benzene	3.97(70) 4.08(a)	5.53(a)		3.35 3.43	3.90 4.02	3.58 3.69	3.65 3.76	3.68	3.66	3.7(d)
2-chlorobiphenyl	4.72(a)	6.32(a)		3.89	4.68	4.32	4.40	4.33	4.23	4.3
2,4,2'4'tetrachloro-biphenyl	6.44(a)	8.38(a)		5.13	6.45	5.95	6.12	6.10	5.87	6.0(d)
quinoline	2.04(46)	3.07(64)		1.96	2.10	1.67	1.72	1.42	1.62	2.2(e)
p-cresol	2.30(46)	3.52(65)		2.15	2.19	1.93	1.98	1.74	1.89	1.9
chlorpyrifos	4.6(a)	6.97(a)	4.24(66)	3.80	4.55	4.20	4.28	4.85	4.70	4.5(d)
2-4-D neutral anion	2.69(29)	4.13(a)	2.82(29)	2.43	2.52	2.31	2.37	1.32	1.37	2.4 1.3
DDT	6.19(67) 5.98(28)	9.79(68)	5.39(28)	4.94 4.80	6.19 5.97	5.78 5.57	5.87 5.66	6.82	6.37	6.0(d)
DEHP	5.3(69)	7.22(69)		4.31	5.27	4.90	4.98	4.24	5.06	5.1(d)

(a) data provided by editors Neely and Blau.

(b) derived via inspection of independent estimates.

(c) log K_{oc} derived via substituent constant is 2.49 (eq 26).

(d) value expected at low sediment concentration ($<10^{-4}$g/ml).

(e) hydrophilic contribution to log K_{oc} expected to be ~ 0.6 (see Karickhoff[55]).

References

1. Macalady, D. L., and Wolfe, N. L., Effects of sediment sorption on abiotic hydrolyses: I. organophosphorothioate esters, submitted to Environ. Sci. Technol., 1982.

2. Pierce, J., and Wolfe, N. L., Effects of sediment sorption on abiotic hydrolyses: II. 4-(p-chlorophenoxy)butylbromide, submitted to Environ. Sci. Technol. 1982.

3. Wolfe, N. L., Effects of sediment sorption on abiotic hydrolyses: III. carboxylic acid esters, in preparation.

4. Zepp, R. G., and Schlotzhauer, P. F., Effects of equilibration time on photoreactivity of the pollutant DDE sorbed on natural sediments, Chemosphere, 10(5), 453, 1981.

5. Mackay, D., Finding fugacity feasible, Environ. Sci. Technol., 13, 1218, 1979.

6. Mackay, D. Fugacity revisited, Environ. Sci. Technol., 16, 654A, 1982.

7. Prausnitz, J. M., Molecular Thermodynamics of Fluid-phase Equilibria, Prentice-Hall International Series in the Physical and Chemical Engineering Sciences, Englewood Cliffs, N.J., 523, 1969.

8. Karickhoff, S. W., Brown, D. S. and Scott, T. A., Sorption of hydrophobic pollutants on natural sediments, Water Res., 13, 241, 1979.

9. Brown, D. S., and Flagg, E. W., Empirical prediction of organic sorption in natural sediments, J. Environ. Qual., 10(4), 382, 1981.

10. Chou, S. J., Griffin, R. A., and Chou, M. M., Effect of soluble salts and caustic soda on solubility and adsorption of hexachlorocyclopentadiene, in Proceedings of the Eighth Annual Research Symposium, U. S. Environmental Protection Agency, EPA-600/9-82-002, Cincinnati, Ohio, 137, 1982.

11. Hassett, J. J., Means, J. C., Banwart, W. L., Wood, S. G., Ali, S., and Khan, A. Sorption of dibenzothiophene by soils and sediments, J. Environ. Qual., 9(2), 184, 1980.

12. Hassett, J. J., Means, J. C., Banwart, W. L., and Wood, S. G., Sorption Properties of Sediments and Energy-related Pollutants, U.S. Environmental Protection Agency, No. EPA-600/3-80-041, Athens, Georgia, 1980.

13. Means, J. C., Wood, S. G., Hassett, J. J., and Banwart, W. L., Sorption of amino- and carboxy- substituted polynuclear aromatic hydrocarbons by sediments and soils, Environ. Sci. Technol., 16(2), 93, 1982.

14. Means, J. C., Wood, S. G., Hassett, J. J., and Banwart, W. L. Sorption of polynuclear aromatic hydrocarbons by sediments and soils, Environ. Sci. Technol., 14, 1524, 1980.

15. Rogers, R. D., McFarlane, J. C., and Cross, A. J., Adsorption and desorption of benzene in two soils and montmorillonite clay, Environ. Sci. Technol., 14(4), 457, 1980.

16. Mingelgrin, U., and Gerstl, Z., Reevaluation of partitioning as a mechanism of nonionic chemicals, J. of Environ. Qual., 12(1), 1, 1983.

17. Bailey, G. W., and White, J. L., Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity, J. Agric. Food Chem., 12, 324, 1964.

18. Bailey, G. W., and White, J. L., Factors influencing the adsorption, desorption, and movement of pesticides in soil, Res. Rev., 32, 29, 1970.

19. Brown, D. S., and Combs, G., A model for predicting sorption of organic cations in soils and sediments, submitted to J. Environ. Qual., 1982.

20. Burchill, S., Greenland, D. J., and Hayes, M. H. B., Adsorption of organic molecules, in The Chemistry of Soil Processes, Greenland & Hayes, eds., Wiley, Chichester, England, 221, 1981.

21. Hance, R. J., Influence of pH, exchangeable cation and the presence of organic matter on the adsorption of some herbicides by montmorillonite, Can. J. Soil Sci., 49, 357, 1969.

22. Harris, C. I., and Sheets, T. J., Influence of soil properties on adsorption and phytotoxicity of CIPC, diuron, and simazine, Weeds, 13, 215, 1965.

23. Harris, C. I., and Warren, G. F., Adsorption and desorption of herbicides by soil, Weeds, 12, 120, 1964.

24. Karickhoff, S. W., and Brown, D. S., Paraquat sorption as a function of particle size in natural sediments, J. of Environ. Qual., 7(2), 246, 1978.

25. Talbert, R. E., and Fletchall, O. H., The adsorption of some s-triazines in soils, Weeds, 13, 46, 1965.

26. Wahid, P. A. and Sethunathan, N., Sorption-desorption of parathion in soils, J. Agric. Food Chem., 26(1), 101, 1978.

27. Wahid, P. A., and Sethunathan, N., Sorption-desorption of α, β, and γ isomers of hexachlorocyclohexane in soils, J. Agric. Food Chem., 27(5), 1050, 1979.

28. Kenaga, E. E., and Goring, C. A. I., Relationship between water solubility, soil sorption, octanol-water partitioning and bioconcentration of chemicals in biota, in Proceedings of the American Society for Testing and Materials, 3rd Aquatic Toxicology Symposium, STP 707, 78, 1978.

29. Rao, P. S. C., Davidson, J. M., Berkheiser, V. E., Ou, L. T., Street, J. J., Wheeler, W. B., and Yuan, T. L, Retention and Transformation of Selected Pesticides and Phosphorous in Soil-water Systems: A Critical Review, U. S. Environmental Protection Agency, EPA-600/3-82-060, Athens, Georgia, 1982.

30. Walker, A., and Crawford, D. V., The role of organic matter in adsorption of the triazine herbicides by soils, in Proceedings from the Symposium of the International Atomic Energy Agency, 2nd Vienna Isotopes and Radiation in Soil Organic Matter Studies, 91, 1968.

31. Karickhoff, S. W., Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils, Chemosphere, 10, 833, 1981.

32. Schwarzenbach, R. P. and Giger, W., Behaviour and fate of halogenated hydrocarbons in ground water, in press.

33. Schwarzenbach, R. P. and Westall, J., Transport of non-polar organic compounds from surface water to groundwater, Environ. Sci. Technol., 15(11), 1360, 1981.

34. Farmer, W. J., A literature survey of benchmark pesticides, Contract No. 68-01-2889, Criteria and Evaluation Div., OPP, U. S. Environmental Protection Agency, Washington, D.C., 1976 (unpublished report).

35. Freeman, D. H., and Cheung, L. S., A gel partition model for organic desorption from a pond sediment, Science, 214, 790, 1981.

36. Yalkowski, S. H. Solubility and partitioning V: dependence of solubility on melting point, J. Pharm. Sci. 70(8), 971, 1981.

37. Yalkowski, S. H., and Valvani, S. C., Solubility and partitioning I: solubility of non-electrolytes in water, J. Pharm. Sci., 69(8), 912, 1980.

38. DiToro, D. M., and Horzempa, L. M., Reversible and resistant components of PCB adsorption-desorption: isotherms, Environ. Sci. Technol., 16(9), 594, 1982.

39. O'Conner, D. J., and Connolly, J. P., The effect of concentration of adsorbing solids on the partition coefficients, Water Res., 14, 1517, 1980.

40. Voice, T. C., and Weber, W. J., Sorption of hydrophobic compounds by sediments and suspended solids in aquatic systems I: theory and background, submitted to Water Res., 1982.

41. Weber, W. J.; Voice, T. C., Pirbazari, M., Hunt, G. E., and Ulanoff, D. M., Sorption of hydrophobic compounds by sediments and suspended solids in aquatic systems II: methods and pilot compound results, submitted to Water Res., 1982.

42. Briggs, G. G., A simple relationship between soils adsorption of organic chemicals and their octanol/water partition coefficients, in Proceedings, 7th British Insecticide and Fungicide Conference, 83, 1973.

43. Briggs, G. G., Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor, J. Agric. Food Chem., 29, 1050, 1981.

44. Bark, L. S., and Graham, J. T., Studies in the relationship between molecular structure and chromatographic behaviour, VIII. The reversed phase thin-layer chromatography of some halogenated phenols and some halogeno-; alkyl-substituted phenols, J. Chrom., 25, 357, 1966.

45. Leo, A. J., Calculation of partition coefficients useful in the evaluation of the relative hazards of various chemicals in the environment, in I. J. C. Symposium on Structure Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms, Veith, G. D., ed., 1975.

46. Leo, A., Hansch, C., and Elkins, D., Partition coefficients and their uses, Chem. Rev., 71(6), 525, 1971.

47. Lambert, S. M., Functional relationship between sorption in soil and chemical structure, J. Agric. Food Chem., 15(4), 572, 1967.

48. Baughman, G. L. and Paris, D. F., Microbial bioconcentration of organic pollutants from aquatic systems--a critical review, CRC Crit. Rev. Micro., 8(3), 205, 1981.

49. Steen, W. C., and Karickhoff, S. W., Biosorption of hydrophobic organic pollutants by mixed microbial populations, Chemosphere, 10, 27, 1981.

50. Carter, C. W., and Suffet, I. H., Binding of DDT to dissolved humic materials, Environ. Sci. Technol., 16(11), 735, 1982.

51. Hassett, J. P., and Anderson, A. A., Effects of dissolved organic matter on adsorption of hydrophobic organic compounds by river and sewage borne particles, Water Res., 16, 681, 1982.

52. Khan, S. U., Adsorption of pesticides by humic substances. A review, Environ. Lett., 3(1), 1, 1972.

53. Parris, G. E., Covalent binding of aromatic amines to humates. 1. reactions with carbonyls and quinones, Environ. Sci. Technol., 14(9), 1099, 1980.

54. Sullivan, J. D., and Felbeck, G. T., A study of the interaction of s-triazine herbicides with humic acids from three different soils, Soil Sci., 106(1), 42, 1968.

55. Karickhoff, S. W., Pollutant sorption in aquatic systems, submitted to J. Environ. Eng. Div.; Proc. ASCE.

56. Rao, P. S. C., Davidson, J. M., and Kilerease, D. P., Examination of nonsingularity of pesticides adsorption-desorption isotherms for soil pesticide systems, Agronomy Abstracts, 34, 1982.

57. Karickhoff, S. W., Sorption kinetics of hydrophobic pollutants in natural sediments, in Contaminants and Sediments, 2, Baker, R. A., ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 193, 1980.

58. Bysshe, S. E., Bioconcentration factor in aquatic organisms, in Research and development of methods for estimating physicochemical properties of organic compounds of environmental concern, part 1, phase II of final report, U. S. Army, Frederick, Maryland, 1981.

59. Neely, B. W., Estimating rate constants for the uptake and clearance of chemicals by fish, Environ. Sci. Technol., 13, 1306, 1979.

60. Spacie, A., Hamelink, J. L., Dynamics of trifluralin accumulation in river fishes, Environ. Sci. Technol. 13, 817, 1979.

61. Yalkowsky, S. H., Valvani, S. C., Water solubility and octanol/water partition coefficients of organics. Limitation of the solubility-partition coefficient correlation, Environ. Sci. Technol, 14, 1227, 1980.

62. Hansch, C.A., Vittoria, C., Silipo, P., Partition coefficients and structure activity relationship of the anesthetic gases, J. Med. Chem., 18, 546, 1975.

63. Chiou, C. T., Peters, L. J., and Freed, V. H., A physical concept of soilwater equilibria for nonionic organic compounds, Science, 206 (16), 831, 1979.

64. Smith, J. H., Mabey, W., Bohonos, W., Holt, B., Lee, S., Chou, T., Bomberger, D., and Mill, T., Environmental Pathways of Selected Chemicals in Freshwater Systems: Part II. Laboratory Studies, U. S. Environmental Protection Agency, EPA-600/7-78074, Athens, Georgia, 1978.

65. Lange, N. A., Handbook of Chemistry, 10th edition, McGraw-Hill Book Co., N.Y., 1967.

66. Macalady, D. L., unpublished data.

67. O'Brien, R. D., Nonenzymic effects of pesticides on membranes, in Environmental Dynamics of Pesticides, Haque, R., Freed, V., eds. Plenum Press, N.Y., 331, 1975.

68. Bigger, J. W., Dutt, G. R., Riggs, R. L., Predicting and measuring the solubility of p,p'DDT in water, Bull. Environ. Contam. Toxi., 2, 90, 1967.

69. Hirzy, J. W., unpublished seminar document, 1978.

70. Watarai, H., Makoto, T., Suzuki, N., Determination of partition coefficients of halobenzenes in heptane/water and 1-octanol/water systems and comparison with the scaled particle calculation, Anal. Chem., 54, 702. 1982.